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Flexible protective diamond-like carbon film on rubber

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In this paper we report an experimental approach to deposit flexible diamond-like carbon (DLC) films on rubber via self-segmentation. By making use of the substantial thermal mismatch between the DLC film and rubber substrate a dense network of cracks forms in the DLC film, contributing to its flexibility. The size of the micro-segments can be controlled by tuning the substrate temperature variation during deposition by varying the bias voltage.

Keywords: DLC film; Crack networks; Flexibility; Rubber substrate

For a rigid protective film deposited on compliant substrates such as rubber, the most critical issues that determine the performance of the entire system are the film flexibility and interfacial adhesion. Sufficient flexibility of the protective film is required to adapt to large deformation of rubber substrates under loading and can be achieved through film segmentation. Strong adhesion is a necessary condition ensuring that the segments of the film adhere well to the rubber substrate, maintaining functionality under loading conditions. In particular, a combination of flexibility and strong adhesion is crucial for DLC films coated on dynamic rubber seals, where cyclic and large elastic deformation may be exerted.

In the past a tile-like structure for films on rubber was proposed and deposited by using a net mask in front of the substrate [1]. Obviously, there are technical problems with this approach: the size of the film segments is rather limited, to the sub-millimeter level, and, especially, the size of the open gap is at least tens of microns (equal to the thickness of the grid). Experimental results revealed that the impact between the asperity of the surface of the sliding counterpart and the sharp edges of open cracks in the films produced a large amount of debris that led to high friction and severe wear of the coated rubber [2]. In this paper we report another approach for depositing micro-segmented DLC films of superior flexibility on rubber. The novelty is that the size of the film segments separated by a close crack network can be well controlled at much smaller length scales. The mechanism of formation of the crack network during deposition and its effects on friction in DLC film-coated rubber are examined and presented.

A hydrogenated nitrile butadiene rubber (HNBR) sheet of 2 mm thickness was used as the substrate in this work. The brown HNBR substrates of 45 × 45 mm size were first cleaned with detergent in an ultrasonic cleaner and then rinsed with demineralized water. Thereafter, wax removal was carried out in an ultrasonic tank with hot demineralized water (90–95 °C) [3]. This washing process with hot water was repeated three times. Next, the HNBR substrates were dried in a centrifuge and then heated up to 120 °C for 15 min in order to evaporate all absorbed water. The substrates were cooled in ambient air to room temperature before being loaded into the deposition chamber. The instrumental modulus of HNBR rubber, as determined by a method described elsewhere [4], was 10.2 MPa and its surface roughness was 0.35 μm measured after wax removal by laser confocal microscopy. The HNBR has a typical coefficient of thermal expansion of $180 \times 10^{-6}\,K^{-1}$.

Plasma cleaning of the rubber substrates and deposition of the DLC films were carried out in a Teer UDP400/4 closed field unbalanced magnetron sputtering system, which consisted of four magnetrons that were all powered off. The HNBR substrates were cleaned by Ar plasma for 30, 35, 40 and 45 min at pulsed dc (250 kHz, 87.5% duty cycle) bias voltages of −600, −500, −400 and −300 V, respectively. During the last 10 min of plasma cleaning hydrogen gas was added (50%) for reactive plasma cleaning to enhance the

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interface adhesion of the DLC films. Immediately after plasma cleaning the DLC films were deposited by plasma chemical vapor deposition (p-CVD) at pulsed dc bias voltages of −300 and −400 V, respectively, for 120 and 60 min to reach the same film thickness of 300 nm. The ratio of gas flow rates was set at $Ar:C_2H_2 = 3:2$, at a constant process pressure of 3×10^{-3} mbar. However, residual hydrogen in the inlet pipeline also used for acetylene could be present for the first 10 min of deposition, during which time growth of the DLC film was minimal. The HNBR substrates were rotated at a speed of 3 r.p.m. during deposition. The substrate temperature during plasma etching/deposition was measured in situ with a thermal couple inserted into the rubber sheet substrate.

The flexibility and adhesion strength of the DLC film were examined via in situ stretch tests on coated specimens of gauge section dimensions 10 × 3 × 2 mm, using a tensile stage installed in a Philips XL-30 FEG scanning electron microscope. The coated rubber sheets were glued onto ∅ 30 mm polished M2 steel discs for the tribology tests. The tests were performed at room temperature (20–23 °C) on a CSM high temperature tribometer with ball-on-disc configuration. The counterpart was a commercial ∅ 6 mm 100Cr6 steel ball of hardness HRC 60–62. All the tribology tests were carried out at a sliding velocity of 10 cm s^{-1} and a constant humidity of 35 ± 1% maintained with a humidity regulator. The surface morphology and wear track of the DLC film-coated rubber after the stretch and tribology tests were characterized by scanning electron microscopy (SEM).

The measured temperature evolution of the rubber substrates during plasma cleaning and successive deposition is shown in Figure 1a. The temperature variation (ΔT) to which the HNBR substrates were exposed during deposition is related to the substrate temperature at the beginning of deposition and the bias voltage used for the p-CVD process. Assuming that the plasma can be considered a 'hot body' whose temperature (T_{plasma}) is constant and merely dependent on the bias voltage applied, the heat flow from the "hot" plasma to the "cold" substrate, which changes the temperature of the substrate as a result, depends on the temperature gradient between the plasma and the substrate. From Fourier's heat conduction equation it follows that:

$$T = (T_0 - T_{plasma}) \times e^{-Kt} + T_{plasma} \quad (1)$$

where T_0 is the initial temperature of rubber substrate. The measured substrate temperatures versus time of plasma treatment (cleaning and deposition) fit Eq. (1) well, as indicated by the solid curves in Figure 1a. By finding the exponential factor K for different rubbers, various amplitudes of ΔT can be readily designed to control the segmentation (as discussed below) by changing the bias voltage against deposition time.

The surface morphology of DLC thin films on HNBR deposited under the condition of varying substrate temperature is characterized by crack networks, as shown in Figure 2. The effective temperature variation during deposition governs the expansion or shrinkage of the rubber substrate and thus the mismatch strain in the growing DLC film, which in turn determines the density of the crack network and the size of DLC film

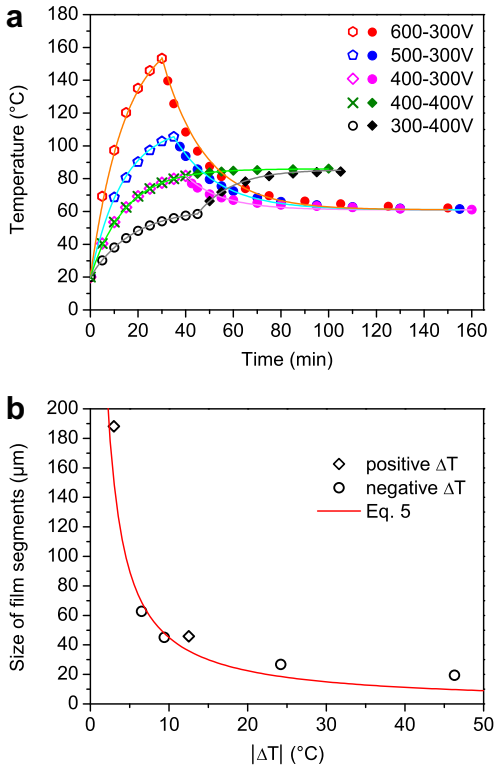

Figure 1. (a) Evolution of measured substrate temperature versus time of plasma cleaning (open symbols) and deposition (close symbols), with the solid curves fitted according to Eq. (1). (b) Sizes of film segments as measured and predicted by Eq. (5) versus temperature variation ΔT during deposition.

segments. It is clear that a positive ΔT or tensile stress in the growing DLC film leads to the formation of a crack network and that the size of film segments is related to the amplitude of ΔT (Figs. 2a and 1b). In contrast, a negative ΔT or compressive stress results in the formation of wrinkles, but also leads to a crack network whose density is likewise governed by the amplitude of ΔT (Figs. 2b and 1b). The different states of deformation are reflected in the morphology of the segments: the film segments formed under tensile misfit stress (positive ΔT) are rather flat (see Fig. 2a), while those generated under compressive stress (negative ΔT) are curved (convex), as shown in Figure 2b. It is anticipated that the cracks originate in the early stage of DLC film growth due to the thermal mismatch strain once a critical thickness is reached [5,6], and grow continuously with increasing film thickness. The result is very interesting, since the segment size of the DLC films is on the micrometer scale and tunable. In this way we were able to control the density of the crack network or wrinkles, without the necessity of using a net mask as proposed in earlier work [1]. In particular, the cracks are close together and their edges bend inwards (see Fig. 2), which is crucial in preventing the formation of a large amount of wear debris that causes wear and high friction in practical applications [2].

The size of the film segments is related to the thermal mismatch strain, which depends on the ΔT to which the rubber substrate is exposed during deposition. The thermal mismatch strain between a DLC film and rubber

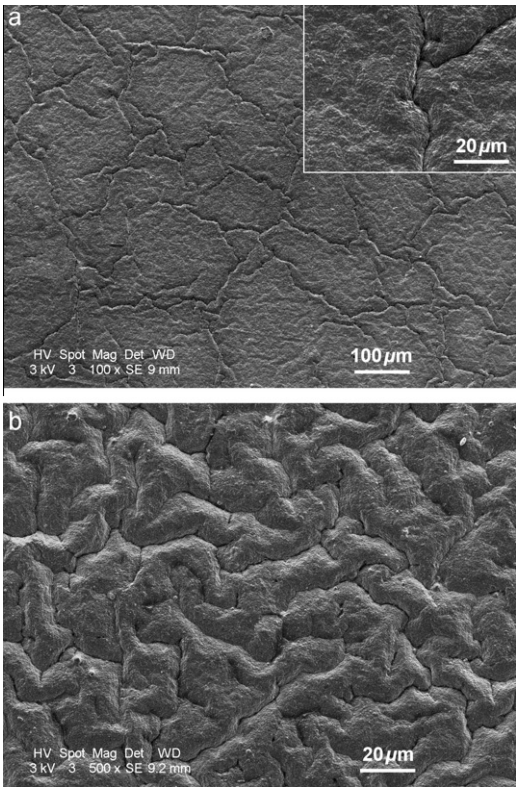

Figure 2. Surface morphology of DLC films on HNBR deposited for different temperature variations: (a) $\Delta T = 3.0$ °C with an inset of higher magnification showing the inward bending crack edges; (b) $\Delta T = -46.3$ °C.

substrate arises due to the considerable difference in their coefficients of thermal expansion (CTE, α) and is usually described by:

$$\Delta\varepsilon = (\alpha_s - \alpha_f)\Delta T \tag{2}$$

where the subscripts f and s indicate the film and substrate, respectively. The crack spacing of a film having identical elastic properties as the substrate can be estimated as [6]:

$$l \cong \frac{5.6}{\varepsilon_0}\sqrt{\frac{\Gamma_f t_f}{\bar{E}}} \tag{3}$$

where Γ_f and t_f are the fracture energy and thickness of the film and ε_0 is the applied strain or mismatch strain. For DLC film-coated rubber, where the two materials have rather different elastic properties, the effective modulus $\bar{E}$ for the equal biaxial stress condition needs to be modified so as to take into account the differences in properties and the thickness ratio between the DLC film and the rubber substrate [7]:

$$\bar{E} = \frac{E_s t_s}{E_s t_s + E_f t_f}\frac{E_f}{1 - v_f} \tag{4}$$

where E is the modulus, v is the Poisson's ratio and t the thickness of the DLC film or rubber substrate.

Inserting Eqs. (2) and (4) into Eq. (3) yields:

$$l \cong \frac{5.6}{(\alpha_s - \alpha_f)\Delta T}\sqrt{\frac{\Gamma_f t_f (1 - v_f)(E_s t_s + E_f t_f)}{E_f E_s t_s}} \tag{5}$$

Table 1. Modulus (E), thickness (t), CTE (α) [9] and Poisson's ratio (v) of HNBR substrate and DLC film.

Properties	HNBR	DLC film
E (MPa)	10.2	150,000
t (μm)	2000	0.3
α ($\times 10^{-6}$ K^{-1})	180	6
v	0.5	0.13

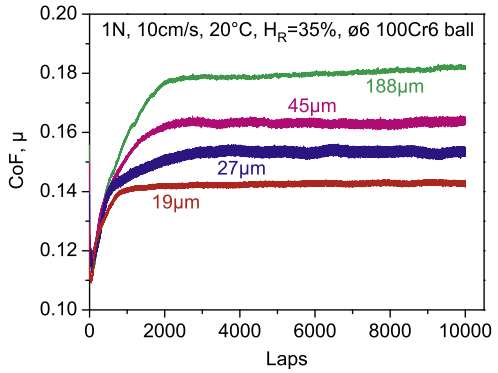

Figure 3. Coefficient of friction of 300 nm thick DLC films on HNBR with segment sizes indicated.

Consequently, the crack spacing is inversely proportional to ΔT, and also related to the fracture energy, effective modulus and thickness of the DLC film. To verify the validity of Eq. (5), $\Gamma_f = 35$ J m^{-2} for DLC films [8] was used (other physical constants are listed in Table 1). We estimated the average crack spacing (equal to the average size of film segments) and good agreement between experiment and theory was obtained (see Fig. 1b).

The density of the crack network or segment size affects the flexibility and consequently the friction of DLC film-coated HNBR rubber. Figure 3 shows the tribological results for DLC films of different segment sizes. Clearly, the DLC films with smaller segments exhibited a lower steady-state coefficient of friction (CoF) and also a shorter time to reach the steady-state CoF. SEM observations (not shown) revealed that the DLC films with larger segment sizes cracked further during sliding against the steel ball. These newly formed individual cracks propagated through the entire segments in a brittle manner and caused the formation of debris that produced wear in both the counterpart and the DLC film itself, leading to greater friction. In contrast, the DLC film with the smallest segment size (19 μm) showed few new cracks under loading, only tiny polished spots on the convex segments after sliding for 10,000 revolutions. More than 95% of the surface area of the DLC film was intact after the tribology test. In situ tension tests measured 8% strain tolerance for the DLC film with the smallest segment size, below which no new cracks were formed under tension. Less than 5% strain tolerance was observed for the DLC film with the largest segment size. Nevertheless, no delamination was observed for any of the DLC films even after the rubber substrates broke down at ~80–90% strain, indicating superior interface adhesion.

In summary, flexible DLC films of micrometer scale segments have been deposited on rubber by self-segmentation. The size of the film segments can be tuned by controlling the temperature variation of the rubber substrate. An analytical description of the crack spacing gives a good estimate of the segment size (equivalent to the crack spacing). Clearly, the dense crack network contributes to the flexibility and ultra-low friction of DLC-coated rubber. The model of and experimental approach to film segmentation have also been applied to other kinds of rubber substrates, including alkyl acrylate co-polymer and nitrile butadiene rubbers, and the results confirm their validity. It can be concluded that this work provides generic design rules for the deposition of flexible and low friction films on dynamic rubber seals and an approach to drastically reduce energy consumption in bearings and other lubrication systems.

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